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SPECIFICATION

RELEASE AGENT FOR METALLIC MOLD

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a release agent for metallic mold for forming a plastic molded product.

2. Description of the Related Art

Plastics have excellent properties such as easy processability, high productivity, light weight and relative low procuring cost, so they are used for the parts and structural materials for automobile, autobiography, scooter, television, radio, audio equipment, washing machine, rice cooker, personal computer, portable telephone, game machinery, building materials, office supplies, stationery, toys, sports goods, sports equipment, agricultural tools and marine tools.

They are usually prepared by plastic processing methods such as injection molding, blow molding, compression molding, transfer molding, rotating molding, slush molding, inflation tubular film process, and extrusion molding.

As plastics processing are conducted at high temperature above 200°C, additives, monomers, decomposed materials in the plastics are changed to carbonized materials such as tar, pitch and other coloured sticky substances, which are apt to adhere to the surface of the screw, bar-

rel , die and metallic mold of the plastic processing machine to cause transfer of the carbonized materials to the molded product.

Above mentioned transfer make the surface of molded product dirty and make the dimensions of the molded product inaccurate, not to perform expected moving or structural function, therefore cleaning the screw, barrel, die and metallic mold of the plastic processing machine has been required.

In case of production change from specific coloured molded article to noncoloured or other coloured molded article, cleaning the screw, barrel and die has been also required to avoid cross contamination caused by remained specifically coloured resin compound.

However there are some problems on the conventional cleaning method of the screw, barrel, die and metallic mold.

There are some problems occurring at releasing the plastic molded product from metallic mold.

The metallic mold for forming the plastic molded product has the complicated shape with fine hollow and convex parts.

Therefore, the plastic molded product such as mechanical parts for electronic device and automobil has the complicated shape, consequently it is difficult to release the plastic mold product from metallic mold, because both surface has the complicated contrasting shape, which causes plastic mold product ingrowing to

metallic mold as if anchor bites the rock of bottom of the sea.

To avoid above mentioned difficulty of releasing both surface, there has been conducted to give activity to the interface between the metallic mold and the plastic molded product.

As the method for giving activity, the lubricant has been conventionally used as the release agent for metallic mold.

The lubricant is usually applied by coating to the metallic mold surface.

However, when the metallic mold coated by the conventional release agent was used for a long time, hard and uneven heterogeneous layer was formed by the following reasons.

One reason is accumulation of the resin and its additives such as antioxidant, metal deactivater, nucleating agent, antiultraviolet agent, antistatic agent, crosslinking agent, vulcanization agent and lubricant.

The other reason is accumulation of the decomposition materials of resin and its additives.

The uneven shape on the surface of metallic mold apt to be transferred on the surface of the plastic molded product and the accumulated contaminants on the surface of the metallic mold are adhered to the surface of the plastic molded product.

Above mentioned trafering of shape makes the dimensions of the plastic molded product unaccurate, not to perform

expected moving or structural function, and adhering of contaminant makes the surface of the plastic molded product dirty.

The hard and uneven heterogenous layer on the surface of the metallic mold surface makes releasing property wrong.

To remove the contaminants and heterogenous layer on the surface of the metallic mold, it is general way to wash the soiled metallic mold after using predetermined time.

At the plastic molded product maker, washing is curried out after troublesome work of taking the soiled metallic mold out from plastic processing machine, and taking the plastic mold to pieces, which requires times and labou to cause heavy loss at efficiency and cost.

Especially at complicated or large size metallic mold, removing, demantling and washing work are tremendous to cause obstacle to improving the productivity and cost down.

To decrease the number of times of the metallic mold washing, a release agent has been employed.

As the release agent, there has been known many types of that such as dimethyl polysiloxane of noncrosslinking type, paraffin wax, higher fatty acid derivative, metal soap, talc, mica and polytetrafluoroethylene of crosslinking type and the like.

However, conventional release agent has been pointed out the following draw-

back.

In case employing noncrosslinking type of release agent, the release agent stay in specific place of the metallic mold to affect bad influence to the plastic molded product.

In case employing crosslinking type of release agent, it exhibits excellent releasing property, however said release agent apt to adhere to the surface of plastic molded product to prevent the uniform painting or adhering treatment, resulting to decrease postprocessability.

In case of requiring sufficient releasing effect to achieve short shot cycle time, the amount of release agent must be increased, resulting to occur the accumulation and degradation of the release agent on the metallic mold, which bring bad influence to the smooth and gross properties and degradation of mechanical strength such as tensile, elongate and antiimpact strength.

Further, it has become the problem that the release agent itself has decomposed by the high temperature heat transfer from the metallic mold.

For instance, dimethyl polysiloxane oil being representative release agent has been gradually decomposed over the temperature of 150°C and has been rapidly decomposed over the temperature of 200°C to form viscous gel like materials, which has become the problem to degrade the releasing property.

For improving the heat-resistant pro-

perty of the said dimethyl polysiloxane, there has been proposed the aminogroup or mercaptogroup modified dimethyl polysiloxane.

However, there has been detected the problem that said modified dimethyl polysiloxane has generated bad smell such as ammonia gas or mercaptan and has coloured the plastic molded product.

Also, dimethyl polysiloxane has been detected its problem that the release agent using dimethyl polysiloxane must has been prepared by dispersing it in the water to form the micelle by using surface active agent, because dimethyl polysiloxane itself is not compatible with water.

The release agent using polytetrafluoroethylene has the drawback that it must be baked onto the surface of metallic mold, therefore many troublesome repeating work of baking must be conducted notwithstanding its excellent releasing effect and secondary processing property.

It is desirable that the release agent for metallic mold is prepared as the emulsion type from viewpoint of cost, toxicity, ignition, handling and applicability.

Emulsion type agent is prepared by the method that surface active agent, water and non-water-soluble dimethyl polysiloxane oil or wax oil is agitated to form micelle, which is able to be dispersed into water.

However, above mentioned surface active

agent reacts with the ingredients bleded from plastic molded product to form the strong membrane (coated layer) on the surface of the metallic mold.

The membrane (coated layer) has hard and uneven heterogeneous shape, therefore the shape is trasferred on the surface of the plastic molded product to cause the problem of procucing the out of standard plastic molded product.

On the other hand, when above mentioned release agent of crosslinked type by baking is used, the baked membrance (coated layer) of exhibiting the releasing effect has been gradually scraped by the resin composition contacting to the metallic mold at each injection shot.

As the above mentioned baked type release agent is gradually scraped at each shot of plastic resin composition into metallic mold, the release agent is removed from the surface of metallic mold by repeating shots from 10 to 20 .

Then from 10 to 20 shots were over, new release agent must be applied onto the surface of metallic mold, which is very troublesome works.

Further above mentioned baked type release agent has the other problem owing to containing the reactive functional group such as amino, mercapto, isocyanate or vinyl group which is used for conducting crosslinking and baking reaction on the surface of metallic mold.

Owing to the reactive functional group, the surface energy of the releasing

agent layer on the metallic mold becomes very large to increase the frictional force between the surface of the plastic molded product and the surface of release agent layer, which causes consumption of the release agent layer by scraping by each injection shot, resulting to restrict the life of release agent layer for the term of from 10 to 20 shots of injection mold.

Short life of the release agent requires often time of the release agent baking treatment, which lead to accumulation of the unnecessary baked crosslinked release agent on the surface of the metallic mold, which affect bad influence such as shape and contaminant transferring to the plastic molded product.

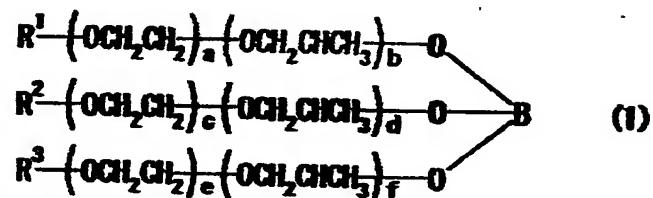
As mentioned above, conventional type release agent has the drawback such as poor release effect, short durability term, difficult secondary processability and difficult treatment (baking) work onto the metallic mold.

SUMMARY OF THE INVENTION

As a result of diligent investigation by the present invention under such situation, the present invention provides a release agent for metallic mold for forming a plastic molded product characterized by containing a borate ester of a polyoxyalkylene.

DETAILED DESCRIPTION OF THE
INVENTION

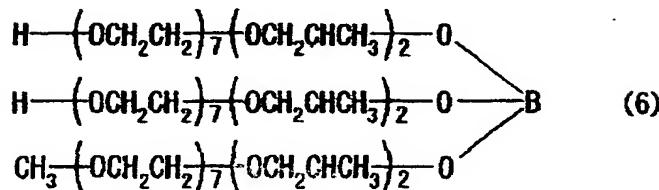
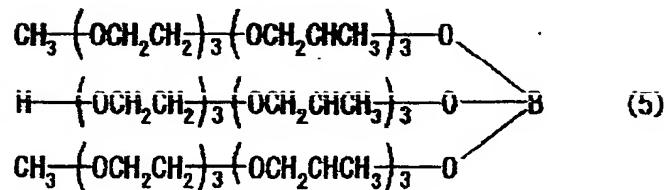
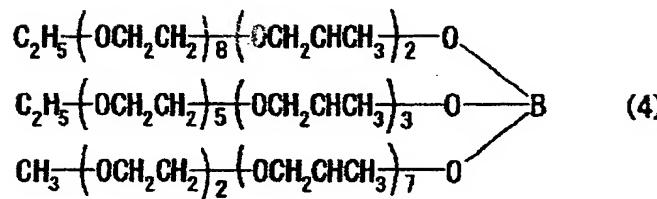
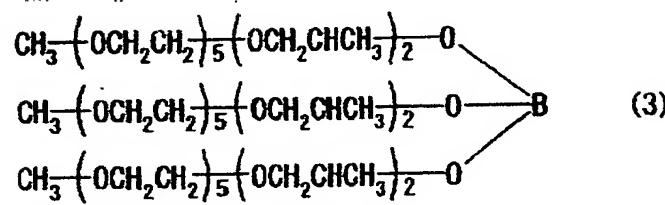
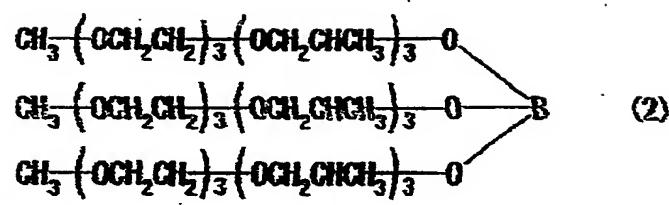
A borate ester of polyoxyalkylene used for the present invention is a chemical compound expressed by the following general formula (1).

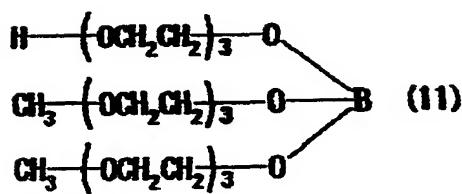
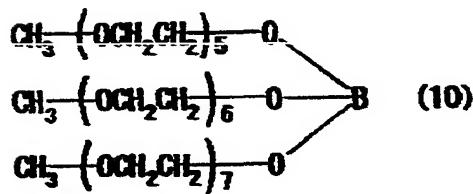
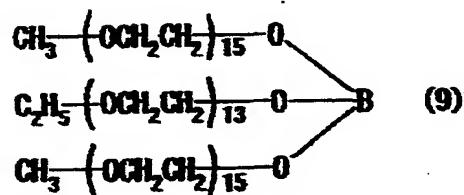
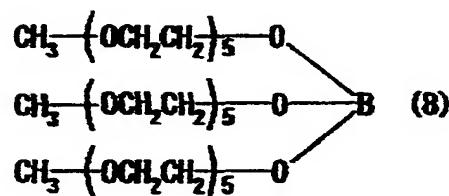
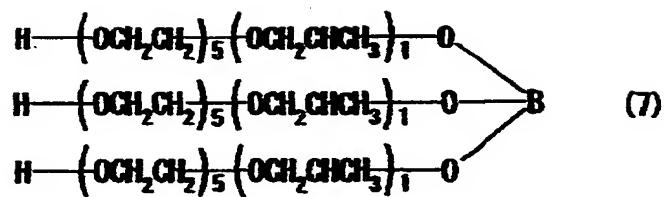


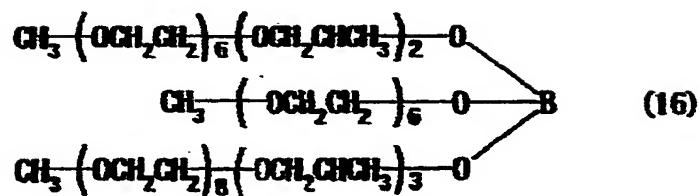
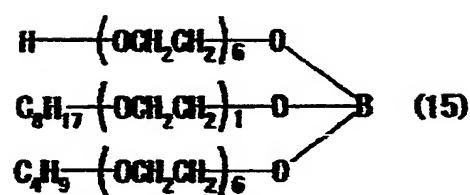
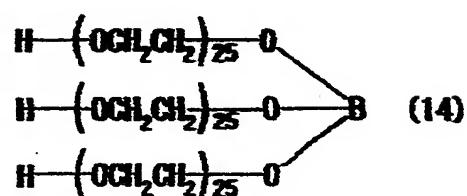
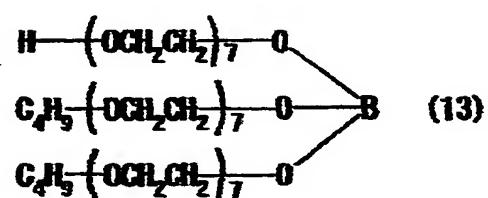
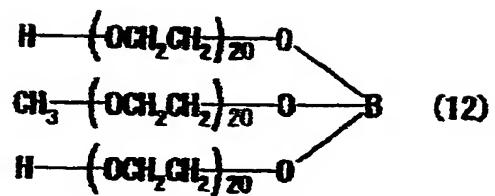
wherein R^1 , R^2 and R^3 are independently selected from group consisting of hydrogen and hydrocarbon group, a , b , c , d , e and f are positive integers independently from 0 to 30 whose sum is from 6 to 80.

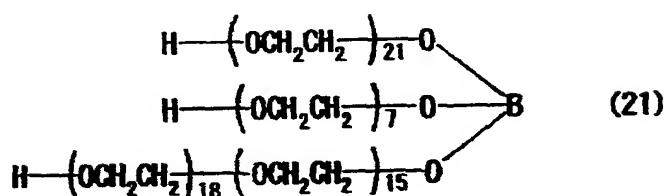
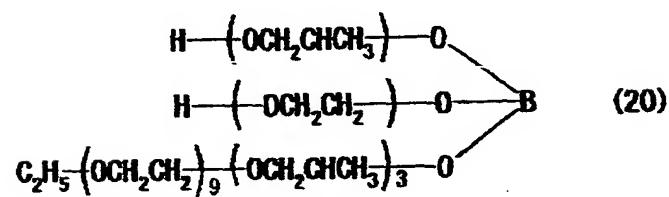
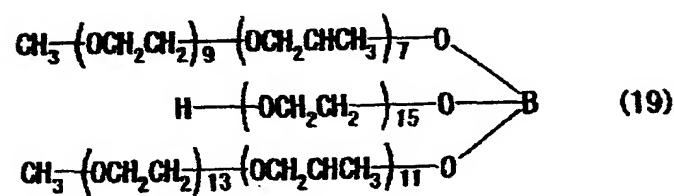
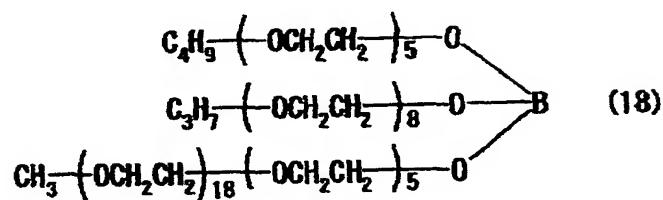
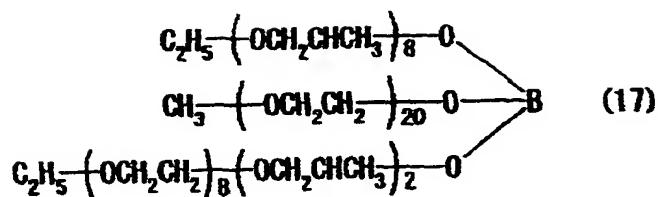
Example of the hydrocarbon group are alkyl group such as methyl, ethyl, propyl, isopropyl, butyl, pentyl, hexyl, octyl, nonyl, decyl, dodecyl, hexadecyl, octadecyl and docosyl groups and phenyl, tolyl and cyclohexyl group.

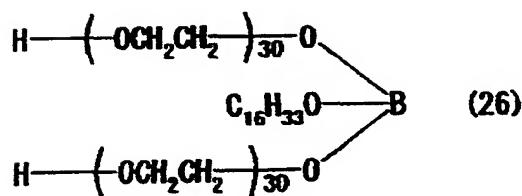
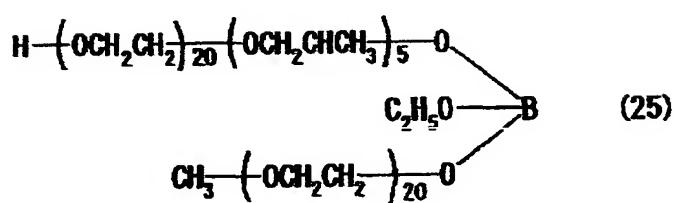
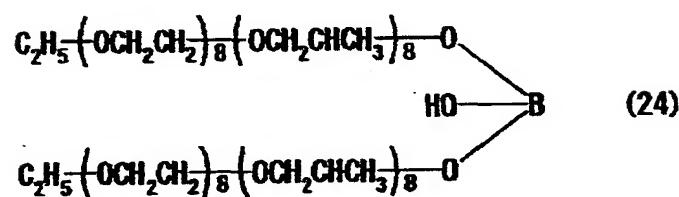
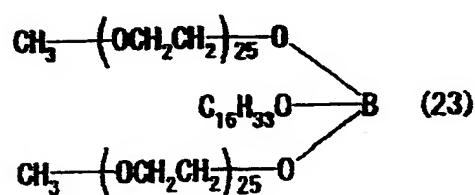
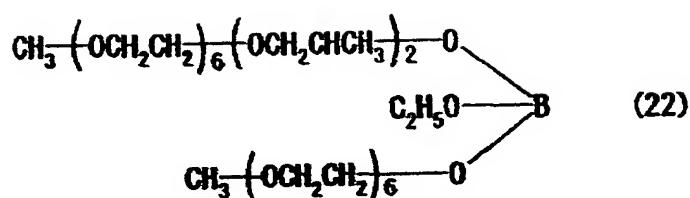
Illustrative of the borate ester of polyoxyalkylene are the chemical compound expressed by the following chemical formula from (2) to (27).

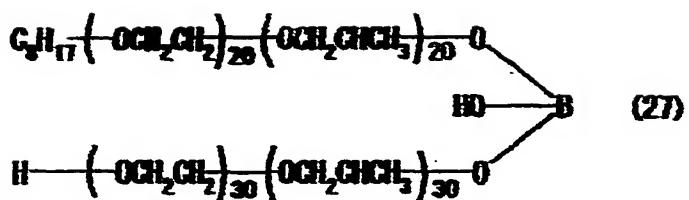












Production method for borate esters of polyoxyalkylene used for the present invention are not limited to specific method, but following method is preferable.

The borate esters of polyoxyalkylene are produced by esterification dehydrogenation or esterexchange reaction by contacting polyoxyalkylene expressed by the chemical formula (28) with boric acid or borate esters of lower alcohol such as methyl alcohol or ethyl alcohol.

It is prefavable that reaction is carried out by using 1 mol of boric acid or borate esters of lower alcohol with from 3 to 3.5 moles of polyoxyalkylene expressed by the chemical fomula (28).

If the mole ratio is less than 3, it is not prefevable because undesirable byproducts of borate esters having two or three boron atoms are generated.

The other byproducts or unreacted polyoxalkylene may be remained in the borate esters unless they do not hinder the purging effect of the resin composition of the present invention.



wherein R¹ and R² are independently selected from group consisting of hydrogen and hydrocarbon group, a and b are independently from 0 to 30.

Example of the hydrocarbon group are alkyl group such as methyl, ethyl, propyl, isopropyl, butyl, pentyl, hexyl, octyl, nonyl, decyl, dodecyl, hexadecyl, octadecyl and docosyl groups and phenyl, tolyl and cyclohexyl group.

Example of the polyoxyalkylene expressed by the chemical formula (28) are as follows.

diethylene glycol monomethyl ether,
diethylene glycol monoethyl ether,
diethylene glycol monoisopropyl ether,
diethylene glycol monobutyl ether,
diethylene glycol monoocethyl ether,
diethylene glycol monodecyl ether,
diethylene glycol monohexadecyl ether,
diethylene glycol monooctadecyl ether,
triethylene glycol monomethyl ether,
triethylene glycol monoethyl ether,
triethylene glycol monoisopropyl ether,
triethylene glycol monobutyl ether,
triethylene glycol monobutyl ether,
triethylene glycol monoocethyl ether,
triethylene glycol monodecyl ether,
triethylene glycol mono hexadecyl ether,
triethylene glycol mono octadecyl ether,

tetraethylene glycol monomethyl ether,
tetraethylene glycol monoethyl ether,
tetraethylene glycol monoisopropyl ether,
tetraethylene glycol monobutyl ether,
tetraethylene glycol monoocethyl ether,

tetraethylene glycol monodecyl ether,
tetraethylene glycol monohexadecyl ether,
tetraethylene glycol monooctadecyl ether,

polyethylene glycol monomethyl ether,
polyethylene glycol monoethyl ether,
polyethylene glycol monoisopropyl ether,
polyethylene glycol monobutyl ether,
polyethylene glycol monoocetyl ether,
polyethylene glycol monodecyl ether,
polyethylene glycol mono hexadecyl ether,
polyethylene glycol mono octadecyl ether,

dipropylene glycol monomethyl ether,
dipropylene glycol monoethyl ether,
dipropylene glycol monoisopropyl ether,
dipropylene glycol monobutyl ether,
dipropylene glycol monoocetyl ether,
dipropylene glycol monodecyl ether,
dipropylene glycol mono hexadecyl ether,
dipropylene glycol mono octadecyl ether,

tripropylene glycol monomethyl ether,
tripropylene glycol monoethyl ether,
tripropylene glycol monoisopropyl ether,
tripropylene glycol monobutyl ether,
tripropylene glycol monoocetyl ether,
tripropylene glycol monodecyl ether,
tripropylene glycol mono hexadecyl ether,
tripropylene glycol mono octadecyl ether,

tetrabutylene glycol monomethyl ether,
tetrabutylene glycol monoethyl ether,
tetrabutylene glycol monoisopropylether,
tetrabutylene glycol monobutyl ether,
tetrabutylene glycol monoocetyl ether,

tetrapropylene glycol monodecyl ether,
tetrapropylene glycol monohexadecyl ether,
tetrapropylene glycol monooctadecyl ether,

polypropylene glycol monomethyl ether,
polypropylene glycol monoethyl ether,
polypropylene glycol monoisopropyl ether,
polypropylene glycol monobutyl ether,
polypropylene glycol monoocethyl ether,
polypropylene glycol monodecyl ether,
polypropylene glycol mono hexadecyl ether,
polypropylene glycol mono octadecyl ether,

diethyleneglycol tripropylene glycol
monomethyl ether,
tetraethyleneglycol dipropylene glycol
monomethyl ether,
tetraethyleneglycol tripropylene glycol
monomethyl ether,
tetraethyleneglycol tetrapropylene glycol
monomethyl ether,
pentaethyleneglycol dipropylene glycol
monomethyl ether,
pentaethyleneglycol tripropylene glycol
monomethyl ether,
diethyleneglycol tetrapropylene glycol
monomethyl ether,

hexaethyleneglycol dipropylene glycol
monomethyl ether,
hexaethyleneglycol dipropylene glycol
monomethyl ether,
hexaethyleneglycol tripropylene glycol
monomethyl ether,
hexaethyleneglycol tetrapropylene glycol
monomethyl ether,

hexaethylene glycol pentapropylene glycol
monomethyl ether,

hexaethylene glycol hexapropylene glycol
monomethyl ether,

heptaethylene glycol dipropylene glycol
monomethyl ether,

heptaethylene glycol dipropylene glycol
monomethyl meth ether,

heptaethylene glycol tripropylene glycol
monomethyl ether,

heptaethylene glycol tetrapropylene glycol
monomethyl ether,

heptaethylene glycol pentapropylene glycol
monomethyl ether,

heptaethylene glycol hexapropylene glycol
monomethyl ether,

heptaethylene glycol heptapropylene glycol
monomethyl ether,

octaethylene glycol dipropylene glycol
monomethyl ether,

octaethylene glycol tripropylene glycol
monomethyl meth ether,

octaethylene glycol tetrapropylene glycol
monomethyl ether,

octaethylene glycol pentapropylene glycol
monomethyl ether,

octaethylene glycol hexapropylene glycol
monomethyl ether,

octaethylene glycol heptapropylene glycol
monomethyl ether,

polyethylene glycol polypropylene glycol
monomethyl ether,

triethylene glycol ,

tetraethylene glycol ,
pentaethylene glycol ,
hexaethylene glycol ,
heptaethylene glycol ,
octaethylene glycol ,
decaethylene glycol ,
tridecaethylene glycol ,
hexadecaethylene glycol ,
eicosaethylene glycol ,
pentacosaethylene glycol ,
triacosaethylene glycol ,

tripropylene glycol ,
tetrapropylene glycol ,
pentapropylene glycol ,
hexapropylene glycol ,
heptapropylene glycol ,
octapropylene glycol ,
decapropylene glycol ,
tridecapropylene glycol ,
hexadecapropylene glycol ,
eicosapropylene glycol ,
pentacosapropylene glycol ,
triacosapropylene glycol ,

triethylene glycol tripropylene glycol,
tetraethylene glycol dipropylene glycol,
tetraethylene glycol tripropylene glycol,
tetraethylene glycol tetrapropylene
glycol,
pentaethylene glycol dipropylene glycol,
pentaethylene glycol tripropylene glycol,
hexaethylene glycol dipropylene glycol,
hexaethylene glycol tripropylene glycol,
hexaethylene glycol pentapropylene
glycol,

hexaethylene glycol hexapropylene glycol,
heptaethylene glycol dipropylene glycol,
triacosaethylene glycol dipropylene
glycol,

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heptaethylene glycol tetrapropylene
glycol,

heptaethylene glycol pentapropylene
glycol,

heptaethylene glycol hexapropylene
glycol,

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glycol,

octaethylene glycol dipropylene glycol,
octaethylene glycol tripropylene glycol,
octaethylene glycol tetrapropylene
glycol,

octaethylene glycol pentapropylene
glycol,

octaethylene glycol hexapropylene glycol,
octaethylene glycol pentapropylene
glycol,

octaethylene glycol octapropylene glycol,
polyethylene glycol polypropylene glycol,

tripropylene glycol triethylene glycol
monomethyl ether,

tetrapropylene glycol diethylene glycol
monomethyl ether,

tetrapropylene glycol triethylene glycol
monomethyl ether,

tetrapropylene glycol tetraethylene
glycol monomethyl ether,

pentapropylene glycol diethylene glycol

monomethyl ether,
pentapropylene glycol triethylene glycol
monomethyl ether,
pentapropylene glycol tetraethylene
glycol monomethyl ether,

hexapropylene glycol diethylene glycol
monomethyl ether,
hexapropylene glycol triethylene glycol
monomethyl ether,
hexapropylene glycol tetraethylene
glycol monomethyl ether,
hexapropylene glycol pentaethylene
glycol monomethyl ether,
hexapropylene glycol hexaethylene glycol
monomethyl ether,

heptapropylene glycol diethylene glycol
monomethyl ether,
heptapropylene glycol triethylene glycol
monomethyl ether,
heptapropylene glycol tetraethylene
glycol monomethyl ether,
heptapropylene glycol pentaethylene
glycol monomethyl ether,
heptapropylene glycol hexaethylene
glycol monomethyl ether,
heptapropylene glycol heptaethylene
glycol monomethyl ether

octapropylene glycol diethylene glycol
monomethyl ether,
octapropylene glycol triethylene glycol
monomethyl ether,
octapropylene glycol tetraethylene
glycol monomethyl ether,

octapropylene glycol pentaethylene
glycol monomethyl ether,
octapropylene glycol hexaethylene glycol
monomethyl ether,
octapropylene glycol heptaethylene
glycol monomethyl ether
octapropylene glycol octaethylene glycol
monomethyl ether
polypropylene glycol polyethylene glycol
monomethyl ether

tripropylene glycol triethylene glycol
monomethyl ether,
tetrapropylene glycol triethylene glycol
monomethyl ether,
tripropylene glycol triethylene glycol
monomethyl ether,
octapropylene glycol diethylene glycol
monomethyl ether,

octaethylene glycol dipropylene glycol
monomethyl ether,
octaethylene glycol tripolypropylene glycol
monomethyl ether,
octaethylene glycol tetrapropylene
glycol monomethyl ether,
octaethylene glycol pentapropylene
glycol monomethyl ether,
octaethylene glycol hexapropylene glycol
monomethyl ether,
octaethylene glycol heptapropylene
glycol monomethyl ether,
octaethylene glycol octapropylene glycol
monomethyl ether,
polyethylene glycol polypropylene glycol
monomethyl ether.

A solvent or diluent may be incorporated into the raw materials such as boric acid, borate ester of lower alcohol and polyoxalkylene, or into borate esters of polyoxalkylene.

If the solvent or diluent are employed, they must not disturb the esterification-dehydration or ester-exchange reaction and their boiling point are preferable below the boiling point of the byproducts or polyoxalkylenes.

Example of the solvent or diluent are ethers such as diethyl ether, dioxane, tetrahydrofuran; aliphatic hydrocarbons such as hexane, acetic anhydride, heptane, octane, nonane, decane, undecane; aromatic hydrocarbons such as benzene, toluene, xylene; cycloalkane such as cyclohexane, cyclohexene; non-proton polar compound such as dimethyl formamide, dimethyl sulfoxide, hexamethyl polyamide phosphate, acetonitrile, N-methyl pyrrolidone; and their chlorine substituted compound such as chloroform and carbon tetrachloride.

A catalysts for the esterification dehydration or ester-exchange reaction may be used.

If the catalysts are necessary for promoting the reaction, following condensation catalysts are recommended.

Example of the catalysts are metallic salt of organic acid such as ferrous octanoate, ferrous naphthenate, cobaltous naphthenate, manganese octanoate, stannum octanoate, stannum naphthenate, lead

octanoate, lead naphthenate, organotin compound such as dibutyl tin diacetate, dibutyl tin dioctanoate, dibutyl tin dilaurate, dibutyl tin dioleate, dibutyl tin dimethoxide, oxidized dibutyl tin; metal alcoholate such as tetrabutyl titanate, tetrabutyl zirconate; titanium chelate such as di-isopropoxy bis-acetyl acetonate titanium, 1, 3-propanedioxy bis-ethyl acetonate titanium, 1, 3-propa-
nedioxy bis-ethyl acetatoacetate titanium; alminum chelate such as alminum acethyl acetonate, alminum tris-ethyl acetatoacetate; amines such as hexyl amine, dodecylamine phosphate, dimethyl hydroxy-amine, diethyl hydroxyamine; tetra ammonium salt such as benzyl hydroxyamine; inorganic acid such as hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid; organic acid such as acetic anhydride, pure acetic acid (over 99.8%), propionic acid, citric acid, benzoic acid, formic acid, acetic acid, oxalic acid, p-toluenesulfonic acid; chlorosilane such as methyl trichlorosilane, dimethyl dichlorosilane; inorganic base such as aqueous ammonia; organic base such as ethylene diamine, triethanol amine; and amino alkylamine.

It is preferable that the esterification dehydration or ester exchange reaction is carried out under the condition of at reduced or atmospheric pressure, from 50 to 250°C temperature, favourably from 100 to 180°C.

During the reaction, removal of bypro-

ducts such as lower alcohol or water can proceed the reaction easily because removal of byproducts proceed the reaction equilibrium to favorable direction of borate ester of polyoxyalkylenes formation.

As to the removal method, azeotropic distillation using azeotropic agent and batch or continuous distillation using distillation tower are preferable.

For the purpose of improving the properties of the borate ester of polyoxyalkylenes, amino group containing compound and/or solvent may be added to said borate esters of polyoxyalkylenes.

Adding the amino group containing compound to the borate ester of polyoxyalkylenes exhibits the suppressing of borate ester hydrolysis and also exhibits rust preventive effect under the condition of existence of water or its vapor.

Examples of the amino-group containing compound include alkylamine, cyclo alkyl amine, alkanol amine, heterocyclic amine, diamine, lactam, cyclic imide and polyamine, which may be used alone or combination selecting from these compound.

As the alkyl amine, there can be used methyl amine, dimethyl amine, trimethyl amine, ethyl amine, diethyl amine, triethyl amine, propyl amine, N, N-di [poly-(4) oxyethyl] hexadecyl amine, dodecyl dimethyl amine, stearamide propyl dimethyl amine, polyoxyethylene (3-30) octadecyl amine, polyoxyethylene (3-30) lauryl

amine, polyoxyethylene (3-30) oleyl amine, polyoxyethylene (3-30) dilauryl amine, polyoxyethylene (3-30) stearyl amine, polyoxyethylene (3-30) alkyl amine, polyoxyethylene (3-30) dialkyl amine, and di(oleoyloxyethyl) hydroxy amine.

As the cycloalkyl amine, there can be used cyclohexyl amine, methyl cyclohexyl amine and ethyl cyclohexyl amine.

As the alkanol amine, there can be used ethanol amine, diethyl hydroxy methyl amine, diethanol amine, dimethyl aminoethanol, triethanol amine, propanolamine, dimethyl 2-hydroxypropyl amine, butanol amine, methyl di(2-hydroxyethyl) amine, tri(2-hydroxyethyl) amine, hydroxymethyl di(2-hydroxyethyl) amine, dibenzil 2-hydroxypropyl amine and cyclohexyl di(2-hydroxyethyl) amine.

As the cycloalkanol amine, there can be used cyclohexanol amine, methylcyclohexanol amine and ethylcyclohexanol amine.

As the heterocyclic amine, there can be used pyridine, lutidine, 3, 4-xylylidine, piperidine, N-methyl piperidine and N-ethyl piperidine.

As the lactam, there can be used propio lactam, N-methylpropio lactam, N-ethyl butyro lactam, N-methyl varero lactam, N-methyl caprolactam and phenyl caprolactam.

As the cyclic imide, there can be used succinimide, N-methyl succinimide, N-ethyl succinimide, phenyl succinimide and 2-undecyl imidazoline.

As the diamine, there can be used ethylene diamine, triethylene diamine and tetraethylene diamine.

As the polyamine, there can be used diethylene triamine, triethylene tetramine and pentaethylene pentamine.

Among these aminogroup containing compound, tertiary aminogroup containing compounds exhibit excellent effect of preventing hydrolysis of borate ester of polyoxyalkylene and promoting the cleaning and purging the coloured contaminants.

Example of tertiary aminogroup containing compounds having above mentioned excellent properties are polyoxyethylene (3-30) octadecyl amine, polyoxyethylene-(3-30) lauryl amine, polyoxyethylene (3-30) oleyl amine, polyoxyethylene (3-30) dilauryl amine, polyoxyethylene (3-30) stearyl amine, polyoxyethylene (3-30) alkyl amine, polyoxyethylene (3-30) dialkyl amine .

The amount of aminogroup containing compound to 100 parts by weight of borate ester of polyoxyalkylene is from 0 to 100 parts by weight, favourably from 5 to 50 parts by weight and most favourably from 10 to 30 parts by weight.

Use of the solvent contributes to lower viscosity of the borate ester of polyoxyalkylene .

As the solvent, there can be used water, methyl alcohol, ethyl alcohol, isopropyl alcohol, butyl alcohol, isopropyl ether, ether, ethylene glycol, polyethylene glycol, polyethylene di-

methyl ester, diethylene glycol, triethylene glycol, ethylene glycol dimethyl ether, diethylene glycol di-methyl ether, diethylene glycol diethyl ether, ethylene glycol dipropyl ether, triethylene glycol dimethyl ether, triethylene glycol monobutyl ether, diethylene glycol monobutyl ether, diethylene glycol diethyl ether, diethylene glycol propyl ether, diethylene glycol dibutyl ether, dimethyl ether, propylene glycol, acetone, methylethyl ketone, furfural, dioxane, methane sulfonate, diethyl ether, tetra hydrofuran, hexane, acetic anhydride, heptane, octane, nonane, decane, undecane, benzene, toluene, xylene, cyclohexane, cyclohexene, dimethyl formamide, dimethyl sulfoxide, hexamethyl triamide phosphate, acetonitrile, N-methyl pyrrolidone, chloroform and carbon tetrachloride and the solvents are used by alone or combination.

The amount of solvent to 100 parts by weight of borate ester of polyoxyalkylene and aminogroup containing compound are respectively from 0 to 100 parts by weight, favourably from 5 to 50 parts by weight and most favourably from 10 to 30 parts by weight.

The other ingredient other than amino-group containing compound and/or solvent may be incorporated to borate ester of polyoxyalkylene for the purpose of improving the properties of the release agent of the present invention.

As the other ingredient, there can be

used stabilizer, neutralizer, antioxidant, ultraviolet absorber, light stabilizer, antistatic agent, lubricant, processability improving agent, filler, dispersing agent, coupling agent, anti-copper rusting agent, blowing agent, nuclear forming agent, anti-forming agent, deformers, colourant, pigment, dyeing agent, carbon black, water tree preventing agent, voltage stabilizer, antitracking agent, organic peroxide, crosslinking agent, disinfectant, antiseptics, antimold agent and antirust agent.

In the present invention, a release agent for metallic mold means the release agent which is coated on the surface of metallic mold used for plastic or gum processing to prevent the adhesion between metallic mold and plastic molded product, resulting to make the plastic molded product easily separate from the metallic mold.

The metallic molds to which the release agent of the present invention is applicable, are used for making the parts and structural materials for automobile, autobicycle, scooter, television, radio, audio equipment, washing machine, rice cooker, personal computer, portable telephone, game machinery, building materials, office supplies, stationery, toys, sports goods, sports equipment, agricultural tools and marine tools by the method of injection molding, blow molding, compression molding, slush molding, fluidized bed coating, flat film extrusion proce-

ssing and the inflation tubular film process.

The material of mold may be metal or ceramics.

Plastics and gum which are processed by using the metallic mold of the present invention are thermoplastics and thermosetplastics as follows.

As the thermoplastic resin, there can be used high density polyethylene, high pressure low density polyethylene such as HP-LDPE, EVA, EEA, Ionomer, olefin vinylalcohol copolymer, LLDPE, VLDPE, polypropylene (PP), polystyrene (PS), acrylonitrile-butadiene-styrene copolymer (ABS), acrylonitrile-styrene copolymer (AS), acrylonitrile-butadiene copolymer, acrylonitrile acrylate-styrene copolymer, polyvinyl chloride (PVC), polyamide, polymethylmethacrylate (PMMA), polyacetal (POM), aminopolyacrylamide, polyarylate, fluorocarbon resin, polyimide (PI), polyamino-bismaleimide (PABI), polyamideimide (PAI), polyetherimide (PEI), bismaleimidetriazine resin (BT), polysulfone, polybutylene terephthalate (PBT), polyethylene terephthalate (PET), polyvinylidene chloride, polycarbonate (PC), polyvinyl acetate, polyvinyl alcohol, polyvinyl ether, polyvinyl formale, modified PPE, modified polyphenyleneoxide (PPO), polyphenylenesulfide (PPS), polyethersulfone (PESF), polyetheretherketone (PEEK), polyarylsulfone (PAS), polymethylpenten (TPX), liquidcrystal-polymer, silicone resin, natural rubber (NR), butyl rubber (IIR), acrylonierile-

butadiene rubber (NBR), chloroprene rubber (CR), styrene butadiene rubber (SBR), butadiene rubber (BR).

As the thermoset plastic resin, there can be used phenolic resin, urea resin, melamine resin, diallyl phthalate resin, epoxy resin, unsaturated polyester resin and the like.

The plastic molded products made by using the above mentioned resins are used for the parts and structural materials for automobile, autobiography, scooter, television, radio, audio equipment, washing machine, rice cooker, personal computer, portable telephone, game machinery, building materials, office supplies, stationery, toys, sports goods, sports equipment, agricultural tools and marine tools.

They are usually prepared by plastic processing methods such as injection molding, blow molding, compression molding, transfer molding, rotating molding, slush molding, inflation tubular film processing and extrusion molding.

The release agent of the present invention is prepared using one or more than one kind of borate ester of polyoxyalkylene.

The release agent may contain amino-group containing compound and/or solvent.

The release agent may further contain surface active agent, pigment, dye, inorganic filler, dripping preventable agent, precipitation preventable agent, antioxidant and deformer.

The release agent may be filled in the aerosol container with propellant.

Coating of the release agent of the present invention on the surface of the metallic mold can be conducted by brushing, spraying, dipping or contacting woven cloth or nonwoven cloth which are immersed with the release agent.

EXAMPLE

Now, the release agent for metallic mold for forming a plastic molded product according to the present invention will be described in further detail with reference to Examples.

However, it shoud be understood that the present invention is by no means restricted by such specific Examples.

Example 1

Borate ester of polyoxyalkylene expressed by chemical formula (5) was obtained by following synthesis process.

In a 7000 ml flask equipped with three inlet pipe and displaced by nitrogen gas were charged 146g (1 mole) of triethyl borate [$B(OC_2H_5)_3$], 1.2g of dibutyl tin dilaurate and 500 ml of benzene.

Subsequently, the solution in the flask was added with 664g (2 mole) of tripropylene glycol triethyleneglycol monomethyl ether und 318g (1 mole) of tripropylene glycol triethyleneglycol under stirring condition to obtain uniform blended solution.

Subsequently, the solution in the flask was stirred for 13 hours at 95°C under the condition of distillation to remove a ethanol and benzene as the by-product to obtain 989g (0. 99 mole) of a borate ester of polyoxyalkylene expressed by chemical formula (5).

In a vessel, 100 parts by weight of a borate ester of polyoxyalkylene expressed by chemical formula (5), 15 parts by weight of triethyl amine and 10 parts by weight of ethanol were blended for 10 minutes under room temperature to obtain the release agent (1).

The release agent (1) was brushed on the surface of metallic mold for injection molding of polyacetal (POM) resin composition (made by Polyplastic Company Ltd.).

Using above mentioned metallic mold and resin composition, injection mold was conducted.

The terms of maintaining the release effect of the metallic mold was about 55 hours, the terms which was very long comparing to conventional release agent as shown in the comparative example 1.

The words "The terms of maintaining the release effect of the metallic mold" means the terms from starting time to stopping time of injection mold, the stopping time which is the time of being observed any one item of phenomenons such as accumulating of dirty materials on the surface of metallic mold, clouding of the surface of the metallic mold,

transferring the shape or contaminant from the metallic mold to the plastic molded product.

Comparative Example 1

According to the same preparation method of Example 1, a release agent (2) consisting 100 parts by weight of high viscosity silicone oil (500 cs at 25°C) and 20 parts by weight of the chlorinated type solvent was prepared.

The same releasing test was conducted according to the same condition of example 1.

The terms of maintaining the release effect of the metallic mold of comparative example 1 was about 10 minutes.

Example 2

Borate ester of polyoxyalkylene expressed by chemical formula (8) was prepared according to the same preparing method (1) except using pentaethylene-glycol ethylether instead of tripropylene-glycol triethyleneglycol monomethyl ether and tripropyleneglycol triethyleneglycol.

Then, a release agent (3) consisting 100 parts by weight of borate ester of polyoxyalkylenes expressed by chemical formula (8) and 20 parts by weight of the pentaethylene-glycol was prepared.

The same releasing test was conducted according to the same condition of

example 1.

The terms of maintaining the release effect of the metallic mold of example 2 was about 48 hours, the terms which was very long comparing to conventional release agent as shown in the comparative example 1.

Example 3

Borate ester of polyoxyalkylene expressed by chemical formula (14) was prepared according to the same preparing method (1) except using pentacosaethyleneglycol instead of tripropylene glycol triethyleneglycol monomethyl ether and tripropylene glycol triethyleneglycol.

Then, a release agent (4) consisting 100 parts by weight of borate ester of polyoxyalkylene expressed by chemical formula (14) and 20 parts by weight of the polyoxyethylene (9) dilauryl amine was prepared.

The same releasing test was conducted according to the same condition of example 1.

The terms of maintaining the release effect of the metallic mold of example 3 was about 65 hours, the terms which was very long comparing to conventional release agent as shown in the comparative example 1.